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Deterioration of Lecithin-adhered Zinc Phosphide Baits in Alfalfa

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ABSTRACT

*A 2·00 (±0·36)% zinc phosphide (Zn_3P_2, CAS no. 1314-84-7) steam-rolled-oat (SRO) groats bait containing 1·04% lecithin vehicle was broadcast in alfalfa (*Medicago sativa*). Samples of bait were collected immediately after broadcast, and 1, 7 and 14 days after exposure to existent agronomic and climatological conditions. Analyses of respective samples yielded 1·80 (±0·36)%, 1·18 (±0·04)%, 1·20 (±0·11)%, and ≤0·26 (±0·05)% Zn_3P_2. A ~10% loss of Zn_3P_2 occurred immediately due to mechanical broadcast; ~33% loss was noted 1–7 days after exposure to pH 6·0 soil and 0·05 cm rainfall; and ≥87% loss of Zn_3P_2 occurred by day 14 following an additional 0·96 cm rainfall. Mechanical, precipitation and soil-acidity factors are viewed to reduce the concentration of Zn_3P_2-grain baits in crop situations. Lecithin-adhered Zn_3P_2 baits showed a relatively rapid decline in concentration of active ingredient (A.I.) after broadcast and exposure to slight moisture — a useful attribute of these baits in areas where hazards to nontarget wildlife are of concern.*

INTRODUCTION

Zinc phosphide (Zn_3P_2) is an acute rodenticide used in agricultural settings (Hood, 1972; Marsh, 1988; Sterner, 1994). Its toxicity is due to the release of phosphine (PH_3) upon reaction with stomach acids; death results from decreased electron transport and failed respiration (Chefurka

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et al., 1976; Hazardous Substance Databank, 1993). Six federal registrations for Zn_3P_2 in agriculture are maintained by the US Department of Agriculture: three are for control of vole (*Microtus* spp.), mice (*Peromyscus* spp.), and prairie dog populations (*Cynomys* spp.) using steam-rolled oats (SRO) or wheat grains in specified crop/rangeland situations (Sterner, 1994).

Primary hazards of Zn_3P_2-grain baits are a concern to gallinaceous birds, passerines and waterfowl (see Johnson & Fagerstone, 1994), and indirect hazards via undigested Zn_3P_2 loads in gastrointestinal (GI) tracts of target species (rodent carcasses) can also be of concern to canids, felids, and raptors (see Johnson & Fagerstone, 1994; Marsh, 1988; Tkadlec & Rychnovsky, 1990). Development of Zn_3P_2 carriers/vehicles with sufficient efficacy and known degradation properties under specified climatological conditions is needed. Short-term efficacious baits that deteriorate rapidly under critical temperature or moisture conditions afford a useful approach to reducing agricultural damage by rodents, while restricting the length of Zn_3P_2 exposure to nontarget wildlife.

Numerous studies have examined the deterioration of Zn_3P_2 baits (Elmore & Roth, 1943; Doty, 1945; Hayne, 1951; Janda & Bosseova, 1970; Hilton *et al.*, 1972; West *et al.*, 1972; Breyl *et al.*, 1973; Pank, 1976; Merson & Byers, 1985; Koehler *et al.*, 1995). Doty (1945) assumed that, because Zn_3P_2 breaks down under wet and acid conditions (hydrolysis), these baits would decompose rapidly in field situations. Hayne (1951) and Janda and Bosseova (1970) attributed the loss of Zn_3P_2 from grain baits to physical weathering — mainly the mechanical factors of rainfall and wind. Hilton and Robison (1972) reported that exposure of baits to acidic/basic soils increases the rate of Zn_3P_2 hydrolysis to PH_3.

More recent studies have confirmed that petroleum-coated, pelletized, and paraffin baits are more resistant to the effects of weathering than grain baits overcoated with oil vehicles (Pank, 1976; Merson & Byers, 1985; Koehler *et al.*, 1995). For example, Koehler *et al.* (1995) reported that four commercial pelletized baits retained $\geqslant 83\%$ Zn_3P_2 16 days after 1·5–4·5 cm of rain. Conversely, in a series of 30-day weathering tests involving 18 formulations, Pank (1976) found that the greatest ($>60\%$), most rapid ($>40\%$ in 10 days) deterioration of Zn_3P_2 occurred in oat groat baits formulated with 3% lecithin and 6% linseed oil.

Chemical analyses documenting Zn_3P_2 loss from grain baits formulated with lecithin:oil vehicles under field conditions are lacking. This paper describes changes observed in the concentration of a 2·0% Zn_3P_2 SRO-groat bait [1·04% lecithin:mineral oil vehicle (Alcolec-S®:Medical Center Mineral Oil, 50% v:v)] after broadcast and 2 weeks weathering in alfalfa under semi-arid conditions.

METHODS AND MATERIALS

Research was conducted at the Hyslop Crop Science Field Laboratory (HCSFL) of Oregon State University (OSU) located ~10 km northeast of Corvallis, OR. The soil was a Woodburn silty-clay loam (pH = 6·0).

During the period of bait exposure (30 September–14 October 1993), mean (±SD) daily maximum and minimum air temperatures were 23·1 (±4·7)°C and 7·5 (±2·6)°C, respectively. Mean (±SD) daily maximum and minimum soil temperatures (5-cm depth) were 24·1 (±3·7)°C and 13·9 (±1·3)°C, respectively. Mean (±SD) daily relative humidity and dew point were 63·9 (±13·8)% and 6·5 (±2·8)°C, respectively. Precipitation totalled 1·02 cm during bait exposure — 0·00 cm, 0·05 cm (0·02 in.), and 0·96 cm (0·38 in.) for the 1, 6 and 7 days between sample collections, respectively.

Bait was prepared (10 September 1995) by the Formulation Laboratory, Product Development Section, Denver Wildlife Research Center (DWRC). The specific bait formulation was; 2·0% Zn_3P_2 (88·8% active ingredient; Bell Laboratories, Inc., Madison, WI), 0·12% pigment black (CAS no. 1333-86-4; Benbow Chemical Packaging Inc., Syracuse, NY), 96·96% SRO groats (Honeyville Grain Co., Honeyville, UT), and 0·52% Alcolec-S® (American Lecithin Co., Woodside, NY) and 0·52% Medical Center Mineral Oil (Hunt Products Co., Inc., Dallas, TX). Except during ground transport to and from HCSFL (inclusive travel dates; 21–22 September 1993 and 15–18 October 1993), when temperatures varied between ~0 and 30°C, bait was stored in temperature-controlled rooms (~20–22°C). Samples of stored bait were collected at the time of preparation (11 September 1993), broadcast (30 September 1993), and study termination (20 October 1993); these were used to document the stability of bait during storage and to measure changes in exposed bait.

To estimate Zn_3P_2 bait concentrations during actual field exposure, bait was passed through a Spyker® broadcast spreader (Mdl. 75; Spyker Spreader Works, N. Manchester, IN, USA) and collected in a large plastic bag (30 September 1993). An immediate post-broadcast sample was collected (~5:00 p.m.) using a paper cup and was sealed in a freezer-tight bag. Next, ~1 kg of the 'broadcaster-run bait' was hand spread onto a ~ 4 × 1 m plot of 1-year-old alfalfa; a ~ 4 × 1 × 0·4 m enclosure (0·6 cm^2 wire mesh) prevented nontarget exposure to the bait. One (1 October), 7 (7 October) and 14 (14 October) days later, 10–13 g samples (dual samples collected on 14 October) of the alfalfa-exposed SRO groats were collected (~5:00 p.m. daily). Individual Zn_3P_2-SRO groats were picked from the ground beneath plants using small tweezers and sealed in a freezer-tight bag.

All bait samples were analyzed by the Analytical Chemistry Section, DWRC, using a gas chromatographic (GC) headspace analysis technique for PH_3 (USDA/APHIS/DWRC Analytical Method 29-A). A 30% sulfuric acid solution was used to hydrolyze Zn_3P_2 during shaking, then head space analysis (PH_3) was performed using a HP 5880 GC (Hewlett-Packard, Ft Collins, CO) with HP flame photometric detector.

RESULTS AND DISCUSSION

The SRO-groats bait was formulated at 2·0% (±0·12) Zn_3P_2 (see Fig. 1). Dry-stored bait samples collected at broadcast and at study termination maintained this concentration for >40 days (samples analyzed on 21–25 October 1993). Temperature variations between ~0 and 30°C during transport had no deteriorating effects on the stored bait — results in agreement with prior reports of Elmore and Roth (1943) and Janda and Bosseova (1970), indicating that practically 'no change' occurs in Zn_3P_2 grain baits under prolonged dry storage.

The sample collected immediately after passage through the Spyker®

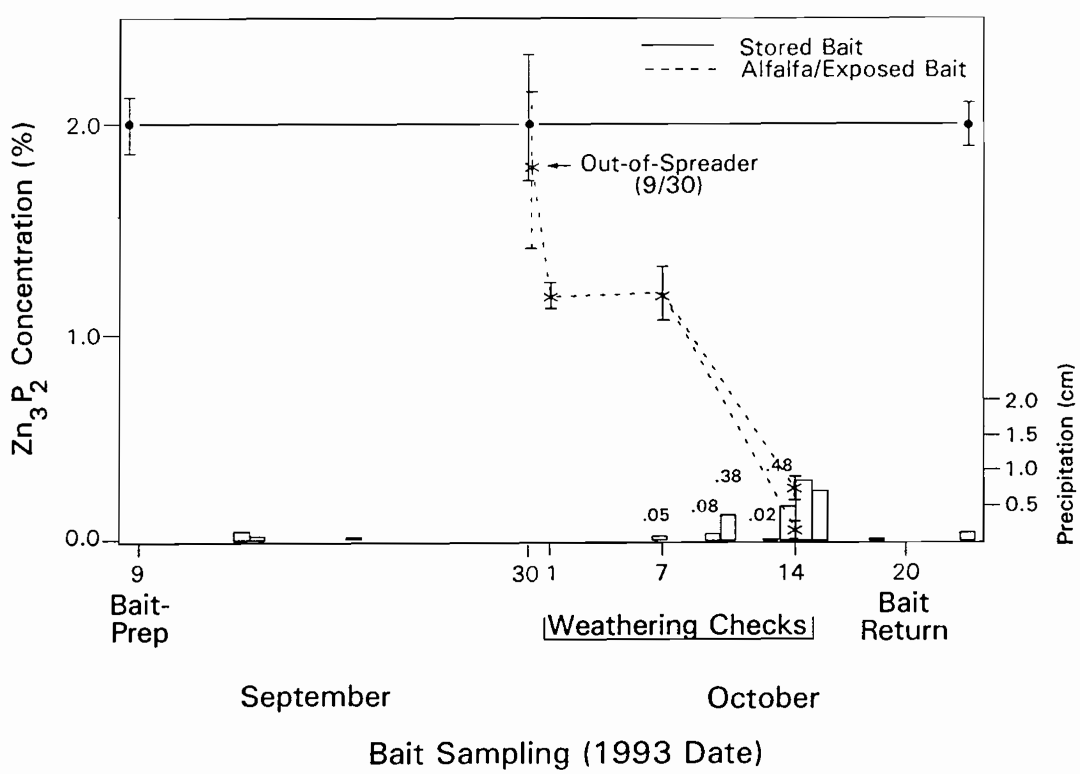

Fig. 1. Mean (±SD) per cent Zn_3P_2 concentrations for stored (solid line) and alfalfa-exposed, weathered bait samples (dashed line) collected on respective dates; daily precipitation (cm) is shown as bars at the base of the plot (right ordinate).

spreader yielded 1·80 (±0·36)% Zn_3P_2; samples collected 1, 7 and 14 days following exposure to alfalfa field conditions contained 1·18 (±0·04)%, 1·20 (±0·11)% and ⩽0·26 (±0·05)% Zn_3P_2, respectively. Together, these data show that: (1) an initial, ~10% loss of Zn_3P_2 [100% − (1·8 ÷ 2·0 × 100)] occurred immediately due to mechanical broadcast — probably the result of some Zn_3P_2 particles being dislodged from the lecithin:oil adhesive by rotor blades, grain abrasions, air movements and grain impacts against the plastic catch bag; (2) ~30% loss {[(1·8 − 1·2) ÷ 2·0] × 100} was noted for samples collected 1 and 7 days post-exposure to pH 6·0 soil and 0·05 cm (0·02 in.) rainfall — data suggesting that initial exposure to slightly acidic soil conditions and ambient dew/humidity probably accounts for a sizable decrease in the potency of 2·0% Zn_3P_2 SRO groats despite negligible precipitation; and (3) ⩾87% loss of Zn_3P_2 {100% − [(0·26 ÷ 2·0) × 100]} was evident for the 14-day samples collected following 7 more days exposure to the 6·0 pH soil and 0·96 cm added rainfall.

Our results generally agree with prior reports of Zn_3P_2 degradation on oil-adhered grain baits following precipitation. Hilton *et al.* (1972) found that bait deterioration was directly related to the amount and intensity of rainfall. In one test, the loss of Zn_3P_2 was correlated with rainfall; ~60% of the rodenticide was removed by 2·5 cm of rain. Similarly, Hayne (1951), using baits of 2% Zn_3P_2 on cracked corn adhered with vegetable oil, reported ~56% loss of Zn_3P_2 during a 27-day period with 5·3 cm precipitation.

The Day 1 decline of ~30% in Zn_3P_2 bait concentration is the lone result that cannot be explained by the 'precipitation effect'. This decline in concentration occurred under arid, essentially non-dew conditions. Mean daily RH and dewpoint temperature on Day 1 (30 September–1 October) were 49·6% and 3·1°C, respectively — an extremely dry day when the minimum temperature (5·2°C) probably exceeded the dewpoint. Perhaps hygroscopic action of Zn_3P_2 or Alcolec-S® accounts for hydrolyzation of surface particles during initial weathering or, as alluded to by Hilton and Robison (1972), local highly acidic pH areas within soils could induce hydrolysis, even with minimal moisture. Interestingly, Koehler *et al.* (1995) observed ~20% loss of Zn_3P_2 in oat baits during the initial 24 h of weathering.

Available data indicate that 'timed reduction' of Zn_3P_2 concentration is a function of mechanical, moisture and soil pH factors during/following baiting, with characteristics of the carrier (grains, pellets, paraffin blocks, etc.) and vehicle (lecithin, corn oil, etc.) determining persistence of the Zn_3P_2 concentration. In the current study, 2% lecithin afforded bait properties of high efficacy, with nearly complete loss of Zn_3P_2 concentration within 14 days post-application under conditions of minimal rainfall. Use of lecithin grain baits and careful timing of bait applications during brief intervals of low rainfall would seem to afford an excellent means of reducing agricultural damage by rodents, while restricting the length of Zn_3P_2-bait exposure to nontargets.

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REFERENCES

Breyl, I., Kredl, F., Holenda, J. & Finala, J. (1973). Decomposition of zinc phosphide in preparations in containers due to climatic influences. *Agrochemia,* **13**(11), 330–332.

Chefurka, W., Kashi, K. P. & Bond, E. J. (1976). The effect of phosphine on electron transport in mitochondria. *Pesticide Biochem. Physiol.,* **6,** 65–84.

Doty, R. E. (1945). Rat control on Hawaiian sugarcane plantations. *Hawaiian Plant Rec.,* **49,** 71–239.

Elmore, J. W. & Roth, F. J. (1943). Analysis and stability of zinc phosphide. *J. Assoc. Official Agric. Chem.,* **26**(4), 559–564.

Hayne, D. W. (1951). Zinc phosphide: Its toxicity to pheasants and effect of weathering upon its toxicity to mice. *Mich. Agric. Exp. Station Q. Bull.,* **33**(4), 412–425.

Hazardous Substance Databank (Databank Online) (1993). Phosphine; CAS no. 7803-51-2. National Library of Medicine, Bethesda, MD, 13 pp.

Hilton, H. W. & Robison, W. H. (1972). Fate of zinc phosphide and phosphine in the soil–water environment. *J. Agric. Food Chem.,* **20**(6), 1209–1213.

Hilton, H. W., Robison, W. H. & Teshima, A. H. (1972). Zinc phosphide as a rodenticide for rats in Hawaiian sugarcane. *Proc. Int. Soc. Sugarcane Technology,* **14,** 561–570.

Hood, G. A. (1972). Zinc phosphide — a new look at an old rodenticide for field rodents. In: *Proc. Vertebr. Pest Conf.*, Vol. 5, pp. 85–92.

Janda, J. & Bosseova, M. (1970). The toxic effects of zinc phosphide baits on partridges and pheasants. *J. Wildl. Mgmt*, **34**(1), 220–223.

Johnson, G. D. & Fagerstone, K. A. (1994). Primary and secondary hazards of zinc phosphide to nontarget wildlife — a review of the literature. US Department of Agriculture/Animal and Plant Health Inspection Service/ Denver Wildlife Research Report. 11-55-005, 26 pp.

Koehler, A. E., Tobin, M. E., Goodall, M. J. & Sugihara, R. (1995). Weatherability of selected zinc phosphide baits in Hawaii. *Int. Biodeter. Biodeg.*, (in press).

Marsh, R. E. (1988). Relevant characteristics of zinc phosphide as a rodenticide. US Forest Service General Technical Report, RM-154, pp. 70–74.

Merson, M. H. & Byers, R. E. (1985). Weathering and the field efficacy of pelletized rodenticide baits in orchards. *Crop Protect.*, **4,** 511–519.

Pank, L. F. (1976). Effects of bait formulations on toxicant losses and efficacy. In: *Proc. Vertebr. Pest Conf.*, Vol. 7, pp. 196–202.

Sterner, R. T. (1994). Zinc phosphide: implications of optimal foraging theory and particle-dose analyses to efficacy, acceptance, baitshyness, and nontarget hazards. In: *Proc. Vertebr. Pest Conf.*, Vol. 16, pp. 152–159.

Tkadlec, E. & Rychnovsky, B. (1990). Residues of Zn_3P_2 in the common vole (*Microtus arvalis*) and secondary poisoning hazards to predators. *Folia Zool.*, **39**(2), 147–156.

West, R. R., Robison, W. H. & Dela Paz, A. M. (1972). Weatherability of zinc phosphide treated rice baits. *Philippine Agric.*, **56,** 258–262.